agreement with the experimental data points indicates that Eq. (C) can adequately describe the results. The dependence of the $O_3$ quantum yield on the flow rate has previously been attributed by Groth[6] to the failure of removing all of the generated ozone, but the present analysis shows that it is inherent to the kinetic mechanism. It is also significant that the ozone quantum yield is a function of the light intensity. However, Eq. (C) predicts that, if $I/v$ can be made sufficiently small by the choice of the flow rate, the production of ozone in $O_2$ at atmospheric pressures provides a suitable 1470-Å actinometer regardless of the intensity of the radiation.

Summarizing briefly, the amount of ozone formed in the 1470-Å photolysis of oxygen has been studied in a flow system as a function of pressure and temperature. At atmospheric pressure, the ozone quantum yield tends toward two, provided the flow rate is sufficiently high. At lower pressures, the ozone quantum yield decreases with decreasing pressure and increasing temperature. These effects are interpreted as arising from the reactions of $^1D$ oxygen atoms. The data are used to derive ratios of the rate constants associated with the individual $O(^1D)$ reactions. On this basis, the reaction of $O(^1D)$ with ozone is found to be fast, whereas those with oxygen and helium are relatively slow.

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# On the Theory of Chemical-Reaction Cross Sections. II. Application to the H + $H_2$ Reaction*

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The statistical–dynamical model formulated in Paper I is applied to the $H+H_2 \rightarrow H_2+H$ reaction and compared with the exact three-dimensional classical-mechanical computer calculations of reaction cross sections. Encouraging agreement is obtained in the low-to-moderate relative velocity range, without the use of adjustable parameters. At very high velocities the comparison indicates the occurrence of some vibrational nonadiabaticity. Calculations are presently in progress to see if this nonadiabaticity equals that expected from a companion paper on analytical mechanics of certain collisions. Applications are also made to several topics: relations between classical and quantum computer calculations of cross sections, between activation energy and the recently reported threshold energy of reaction ($D+H_2 \rightarrow DH+H$), and tests of activated-complex theory.

## I. INTRODUCTION

IN Paper I a statistical–dynamical theory was formulated for chemical-reaction cross sections.[1] It is applied in the present paper to the $H+H_2 \rightarrow H_2+H$ reaction. Extensive computer studies have been made for this reaction by numerical integration of the classical-mechanical equations of motion, both for the case of three atoms on a line[2] and for actual collisions in three dimensions.[2,3] In the latter study[3] reaction cross sections $\sigma_{vjv}$ were calculated for various rotational states of $H_2$ ($j=0$ to 5), for one vibrational state of $H_2$ ($v=0$), and for various initial relative velocities ($V_R=0.9\times10^6$ to $2.0\times10^6$ cm sec$^{-1}$). A comparison of these computer results with the theory of Paper I is given below.

## II. EQUATIONS

In Paper I the activated-complex concept was used, in conjunction with statistical–dynamical postulates, whose possible dynamical origin is discussed in a later paper:

(i) quasiequilibrium postulate for population of activated complexes,

(ii) adiabaticity of some degrees of freedom, where appropriate, and

(iii) a reaction probability postulated to be a function of the excess energy along the reaction coordinate. (The excess is the initial relative translational energy minus the energy of the reaction barrier.)

In (iii) the barrier consists of the natural barrier, the centrifugal barrier, and the contribution from the adiabatic coordinates. The quasiequilibrium postulate (i) is the following: In an ensemble of reacting pairs having a given energy, a given total angular-momentum quantum number $J$ (rotation plus orbital), a given quantum number $v$ for the adiabatic degrees of freedom, and a uniform distribution over all $\mathfrak{N}$ quantum states consistent with this description, the *a priori* probability of finding the pair in any quantum state near the activated-complex region is $1/\mathfrak{N}$. Weaker forms of this postulate were obtained by summing over $J$, or over $v$,

* Supported by a grant from the National Science Foundation.

[1] R. A. Marcus, J. Chem. Phys. **45**, 2630 (1966).

[2] F. T. Wall, L. A. Hiller, Jr., and J. Mazur, J. Chem. Phys. **29**, 255 (1958), and subsequent papers.

[3] M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys. **43**, 3259 (1965).

or over both, for all $J$ and $v$ consistent with the given energy.[4]

Postulates (i) to (iii) were used to obtain an integral equation which was, in turn, solved to obtain an expression for the reaction cross section as a function of the relative velocity and of the initial state of reactants. The equations for the reaction of particular interest here are given below, namely for an atom reacting with a diatomic molecule to form an assumed linear activated complex, the system having one adiabatic vibration during the collision.[5] This adiabatic vibration is the degree of freedom which is an $H_2$ vibration in the $H_2$ and which goes over into a symmetric stretching vibration in the $H_3$ activated complex.[6]

The rotations were treated classically. We quote the equations [Eq. (1) outside of the threshold region and Eq. (2) inside] in a form which neglects rotation–vibration interaction. The latter is included, however, in the original equations (15) and (25) of Ref. 1 from which (1) and (2) were obtained as particular cases. Outside of the threshold region

$$\sigma_{vjp}=(\Gamma\pi\hbar^2/2\mu E_p)\,(I^+\sigma/I\sigma^+)[N^+_{vib}(E_p-V_e)], \qquad (1)$$

and at the threshold,

$$\sigma_{vjp}=(\Gamma\pi\hbar^2/2\mu E_p)[(I^++I)\sigma/I\sigma^+] \times[N^+_{vib}(E_p-V_e-E_j^+)]. \qquad (2)$$

In these equations $\Gamma$ represents a summation over all geometrically isomeric and optically isomeric reaction paths. $\mu$ is the reduced mass of the two reactants. $I^+$ and $I$ denote the moments of inertia of the linear activated complex and of the diatomic reactant, respectively. $\sigma^+$ and $\sigma$ are the symmetry numbers. $N^+_{vib}(y)$ is the number of bending vibrational quantum states having an energy equal to or less than $y$ in the activated complex. $E_j^+$ is $(I/I^+)E_j$, where $E_j$ is the rotational energy of the reactant. $E_p$ is the initial translational energy in the center-of-mass system. $V_e$ is an energy barrier, given by

$$V_e=\epsilon_v^+-E_v, \qquad (3)$$

where $E_v$ is the vibrational energy of the adiabatic modes of the reactants and $\epsilon_v^+$ is the sum of the vibrational energy of the adiabatic modes of the activated complex $E_v^+$ and the potential energy of the (reaction coordinate) $q^r$ motion.[7] ($\epsilon_v^+$ is the minimum energy—aside from the external centrifugal contribution—needed to pass through the set of activated-complex configurations.) A possible correction to Eqs. (1) and (2) for an expected nonadiabaticity when the velocity along $q^r$ is too high in the curved region is discussed later.

Equations (1) and (2) are compared below with classical-mechanical computer calculations of $\sigma_{vjp}$. A quantum-mechanical treatment of the $q^r$ motion leads to the presence of a transmission coefficient, but we omit the equations[1] for a quantum $q^r$ motion here.

When the bending vibrations are treated classically, $N^+_{vib}(y)$ equals $\mathbf{m}^2/2h^2$, where $\mathbf{m}$ is the maximum value of the classical vibration action $\oint pdq$ corresponding to the energy $y$. It is essentially equal to $(m+1)h$, where $m$ is the principal quantum number for the doubly degenerate bending vibration (Appendix I).

## III. APPLICATION TO THE H + $H_2$ REACTION

The sum of the cross sections for the reaction A+BC→AB+C and →A+BC was tabulated[3] for the conditions cited earlier. This sum can be obtained from (1) to (4) by taking $\sigma=\sigma^+=1$ and $\Gamma=2$; there are two geometric isomeric paths, and A, B, and C are distinguishable in the calculation.

### A. Threshold

The potential energy $V_0$ at the saddle point of the linear complex was 9.13 kcal mole$^{-1}$.[3] The change in vibrational energy $E_v^+-E_v$, in the adiabatic vibration was the difference of zero-point energy, 3.08 kcal mole$^{-1}$.[3] Thereby, $V_e$ in Eq. (3) is 6.05 kcal mole$^{-1}$. The threshold energy is the value of $E_p$ for which $\sigma_{vjp}$ exceeds some preassigned amount. For example, at $j=0$ this $E_p$ is 6.89 and 6.93 kcal mole$^{-1}$ according to a least-squares equation,[3] when the preassigned $\sigma$ is 0.010 and 0.033 a.u., respectively [1 a.u.$=\pi(0.529$ Å$)^2$]. [However, the accuracy of this six-constant equation over this very small part of the range (5 a.u.) of $\sigma_{vjp}$ values is not clear.] The corresponding values of $E_p$ computed from Eq. (2) are 6.35 and 6.60 kcal mole$^{-1}$, respectively. The mean difference of about 0.4 kcal mole$^{-1}$ is not far from the corresponding difference of 0.3 kcal mole$^{-1}$ for the one-dimensional case[3] of all three atoms on a line, and might be due to a small nonadiabatic internal centrifugal effect.[6b]

The difference in effective threshold energies for the $j=0$ and $j=5$ cross section is, according to (2), expected to equal the value of $(I/I^+)E_j$, which is about 0.9 kcal mole$^{-1}$. The computer value of about 0.7 kcal mole$^{-1}$ is fairly close to this value. (For accuracy limitation of the 0.7, however, see above.)

### B. Cross Sections

Outside of the threshold region the computer-calculated plots of $\sigma_{vjp}$ versus relative velocity $V_R$ for $j=0$ to $j=5$ were virtually superimposable, particularly

[4] Compare use of a similar postulate in unimolecular reaction rate theory for a local quasiequilibrium between energized molecules and activated complexes of the same $J$ and $E$ [R. A. Marcus and O. K. Rice, J. Phys. & Colloid Chem. **55**, 894 (1951); R. A. Marcus, J. Chem. Phys. **20**, 359 (1952); **43**, 2658 (1965)].

[5] R. A. Marcus, J. Chem. Phys. **43**, 1598 (1965).

[6] (a) For a summary of evidence based on analysis of computer results see Footnote 8 of Ref. 6(b); (b) R. A. Marcus, J. Chem. Phys. **45**, 4500 (1966); (c) **45**, 4493 (1966); (d) (to be published).

[7] When proper coordinates are used, the energy can be written as the sum of various contributions, though the parameters appearing in the properties of the adiabatic modes may vary with position along the reaction coordinate.[6b]

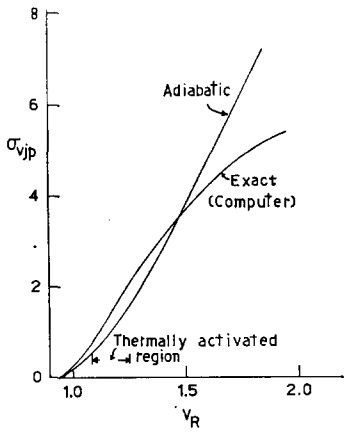


FIG. 1. Total reaction cross section $\sigma_{vjp}$, for all paths, versus relative velocity of reactants $V_R$. Reaction: $H+H_2 \rightarrow H_2+H$ at $j=3$. Exact results: Ref. 3 (computer trajectories). Second curve: Eqs. (1) and (2). Units: $\sigma_{vjp}$ (atomic units), $V_R$ (units of $0.979\times10^8$ cm sec$^{-1}$).

when the scatter in the computer calculations is taken into account. A least-squares fit of the computer results for $j=3$ is plotted in Fig. 1.

Similarly, Eqs. (1) and (2) yield very similar plots for $j=0$ to $j=5$, except at threshold. In Fig. 1 the $\sigma_{vjp}$'s calculated from Eqs. (1) and (2) are plotted for $j=3$, taking the anharmonicity of the bending modes into account (see below). In the threshold region, Eq. (2) should be used, while above the region (1) should be used. For $j=3$ they yield the same answer at $V_R\cong1.2$, and we have used (2) for smaller $V_R$'s and (1) for larger ones for simplicity.[8]

At incident translational energies not far from threshold, the harmonic treatment of the bending vibrations is adequate. However, at high energies anharmonicity should be included in computing the function $N^+_{\rm vib}(E_p-V_e)$ in Eq. (1). The quartic anharmonicity used in the plot in Fig. 1 was estimated from the value of the saddle-point potential energy given[3] for bond angles of $\pi$, $5\pi/8$, and $\pi/3$. The function $N^+_{\rm vib}$ was then calculated with the aid of some recent results on the energy of an anharmonic oscillator as a function of its quantum number[9] and action (Appendix I). In this way $N^+_{\rm vib}(y)$ was found to have a somewhat lower value than the harmonic value, since the actual anharmonic bending oscillators were stiffer than the harmonic ones. At the highest velocity, the difference in $N^+_{\rm vib}(y)$ was only 35%, and was less at lower velocities.

The agreement between Eqs. (1) and (2) and the computer results is seen to be reasonably good, when the absence of arbitrary or adjustable parameters is taken into account. In the moderate velocity range (this range is the one of typical thermal interest[10]) of about 1.1 to 1.2$_5$ the curve based on Eqs. (1) and (2) is slightly lower than the computer one. There is some tendency for the two curves to diverge at high velocities.

The deviation at thermal velocities is rather small. It is about the same as that found in the test of the quasiequilibrium hypothesis,[12] and so is not due to the dynamical postulates. If it is due to neglect of rotation–vibration and other anharmonic interactions, Eqs. (15) and (25) of Ref. 1 could be used to calculate $\sigma_{vjp}$. One would introduce into those equations the value of a function $\omega^+$ appropriate for the case when these interactions are included.

The divergence of the two plots at high $V_R$'s leads to a ratio of apparent limiting values[13] of a factor of about 3 (Appendix II). At high $V_R$'s the approximation of adiabaticity for the symmetric stretching mode of $H_3^\ddagger$ must break down: When the system strikes the curved part of the reaction path in the usual center-of-mass plot of potential-energy contours for linear collisions, translational energy is converted to vibrational energy of this mode in excess of the adiabatic change.[6b–d] This extra energy is "locked in" and so is unavailable for distribution among the bending modes. Thus, the excess energy, $E_p-V_e$ in Eq. (1), estimated on an adiabatic basis is too high at high $V_R$'s and so $N^+_{\rm vib}(E_p-V_e)$ and $\sigma_{vjp}$ are correspondingly too high.

One might conjecture that Eq. (1) may still be applicable, provided $E_p$ is not too large, but that the value used for $\epsilon_v^+$ in (3) should be that computed from an equation which includes the nonadiabatic correction [Eq. (33) of Ref. 6(b)]. Computations of nonadiabatic contributions are in progress. However, an independent analysis of this point can be made by examining the distribution of vibrational energies in the symmetric stretching mode in the activated-complex region, presently hidden in the computer-calculated trajectory studies.

[8] An integral equation bridging the gap between (1) and (2) was actually given in Ref. 1 but not solved. Since the difference between (1) and (2) is minor the alternative approximate procedure is quite adequate.

[9] S. I. Chan, D. Stelman, and L. E. Thompson, J. Chem. Phys. **41**, 2828 (1964).

[10] The rate constant for a given state $v$ varies as

$$\sum_i \int_{E_p} f dE_p,$$

where $f$ is $E_p\sigma_{vjp}\exp[-(E_p+E_i)/RT]$. (Compare Eliason and Hirschfelder.[11]) The thermal average of $E_p$ is therefore

$$\sum_i \int_{E_p} E_p f dE_p \Big/ \sum_i \int_{E_p} f dE_p.$$

Introduction of Eq. (1) and the harmonic approximation for $\sigma_{vjp}$ yields $\langle E_p\rangle = V_e+3RT$ when $V_e \gg RT$.

[11] J. O. Hirschfelder and E. Wigner, J. Chem. Phys. **7**, 616 (1939); M. A. Eliason and J. O. Hirschfelder, *ibid.* **30**, 1426 (1959); L. Hofacker, Z. Naturforsch. **18a**, 607 (1963); R. A. Marcus, J. Chem. Phys. **43**, 1598 (1965).

[12] R. A. Marcus, J. Chem. Phys. **45**, 2138 (1966).

[13] Expression (1) certainly leads to a limiting value: At high energies the configuration space contribution to $N^+_{\rm vib}$ becomes constant because then the bending mode becomes essentially a rotation. The harmonic equation, Eq. (2), leads to a $\sigma_{vjp}$ which increases indefinitely with energy since the configuration space contribution increases with energy without limit for a harmonic oscillator.

Even at low energies there is some nonadiabaticity, which should give rise to a nonadiabatic leak; that is, there will be a small but finite cross section for reactions in which the symmetric stretching mode of the activated complex has an action even as small as zero rather than that of the initial $H_2$ vibration. A quantitative classical and quantum-mechanical treatment of that effect has been given elsewhere.[6b,c] Using it, it should be possible to calculate the "nonadiabatic tail" of the $\sigma_{vjp}$ versus $V_R$ plot at energies below "threshold," and compare with the tail observed[3] in the computer studies.

## IV. COMPARISON OF QUANTUM AND CLASSICAL CROSS SECTIONS

The computer problem of exact calculation of reaction cross sections for the quantum-mechanical system is more formidable than that for the classical-mechanical one. Indeed, only one quantum study for a chemical reaction has appeared, and in that study only several transmission coefficients have been reported thus far.[14] Some comparison of the quantum and classical forms of Eqs. (1) and (2) is of interest, therefore, particularly since a question which lies at the heart of any justification of activated-complex theory also arises here.

When only the symmetric stretching and bending modes are treated in a quantum manner, the ratio of quantum to classical cross sections is

$$\sigma_{vjp}(\text{quantum})/\sigma_{vjp}(\text{classical}) = N^+_{\text{vib}}(\text{quantum})/N^+_{\text{vib}}(\text{classical}), \quad (4)$$

according to Eqs. (1) or (2).

We assume for $N^+_{\text{vib}}(\text{quantum})$ that the bending modes are fully quantized in the activated complex. It should be noted, however, that although there is a good reason for such quantization of the symmetric stretching mode (vibrational adiabaticity plus initial quantization implies subsequent quantization),[11] the question is still moot for the bending modes: Unlike the stretching mode they arise not from vibrations but from a combination of orbital and rotational modes of the reactants. Suitable quantum-mechanical computer studies will resolve this question of the extent of quantization of the bending modes. An analytical mechanical discussion is given in a later paper.[6d]

The ratio in (4) tends to unity as the energy is increased. At low energies the harmonic-oscillator approximation may be used. $N^+_{\text{vib}}(\text{quantum})$ is $\sum(N+1)$, where $N$ is the principal quantum number of the degenerate oscillator and varies in the sum from 0 to its maximum $M$ for the given energy available, $y$. The sum equals $\frac{1}{2}(M+1)(M+2)$, therefore. $N^+_{\text{vib}}$ (classical) is $y^2/2(h\nu)^2$, where $\nu$ is the bending frequency. If a continuous variable $M_c$ is defined by the relation $y=(M_c+1)h\nu$, $M$ agrees exactly with $M_c$ when $M$ is an integer. We have

$$\sigma_{vjp}(\text{quantum})/\sigma_{vjp}(\text{classical}) = (M+1)(M+2)/(M_c+1)^2. \quad (5)$$

This ratio is zero until the excess energy equals the zero-point energy $h\nu$ for this degenerate vibration, 2.8 kcal mole$^{-1}$ according to the surface used earlier.[3] The ratio in Eq. (5) is then 2 and the quantum $\sigma_{vjp}$ is about 0.6 a.u. according to Eqs. (1) or (2). If the threshold energy were defined as one for which $\sigma_{vjp}$ exceeded 0.01 a.u., as suggested by Karplus *et al.*[3] for purposes of tabulation of their computer data, the difference in quantum and classical threshold energies at $j=0$ would be about $(2.8-0.3)$, i.e., 2.5 kcal mole$^{-1}$. If the experimental threshold energy were defined as that energy for which $\sigma_{vjp}$ exceeded 0.2 a.u. (say), the difference in quantum and classical threshold energies would be $(2.8-1.5)=1.3$ kcal mole$^{-1}$.

The plots of $\sigma_{vjp}$ versus $V_R$ for the quantum and classical treatments are otherwise fairly similar though the former has a staircase shape and the latter is a smooth curve which passes through the centers of the stair risers. The usual splitting of degeneracies rounds the staircase edges somewhat.

For the $H+H_2$ reaction the difference in quantal and classical behavior should be most noticeable at temperatures below 1000°K, say, where the difference in threshold energy is comparable to or greater than the thermal energy $RT$.

## V. ACTIVATION ENERGY AND THRESHOLD ENERGY

When a classical description suffices for the bending modes, $\sigma_{vjp}$ in the region near threshold varies as the second power of the energy excess, according to Eqs. (1) and (2). The threshold energy is then quite sensitive to the sensitivity of the experimental detection system. Indeed, for an extremely sensitive detector the nonadiabatic leak discussed in a preceding section would also give a long tail to the observed behavior. According to Eqs. (1) or (2) the quantum $\sigma_{vjp}$ is less sensitive than the classical one to detection limits when zero-point effects are appreciable, because of the staircase nature of the $\sigma_{vjp}$(quantum)-vs-$V_R$ plots.

As another example of application of these equations, we consider the relation between threshold energy for reaction and the activation energy, when the zero-point vibrational energies are large in the threshold studies. Most systems are then present in their ground vibrational states. Let $\frac{1}{2}h\nu_1$, $\frac{1}{2}h\nu_1^+$, $h\nu_2^+$ be the zero-point energies of the reactant, of the symmetric stretching mode of the activated complex, and of the doubly degenerate bending mode of this complex, respectively. According to Eq. (1) and the preceding discussion for

[14] E. M. Mortensen and K. S. Pitzer, Chem. Soc. (London) Spec. Publ. **16**, 57 (1962).

the quantum behavior, the threshold energy $\Delta$ is

$$\Delta = V_0 + \tfrac{1}{2}h(\nu_1^+ - \nu_1 + 2\nu_2^+) + E_j^+. \quad (6)$$

The activation energy $E_a$ is the average energy of the molecules that do react, $\langle E^+ \rangle$, minus that of all the reactant molecules.[15] $\langle E^+ \rangle$ is also equal to the average energy of the activated complexes: translation along reaction coordinate, $RT$; vibration, $\frac{1}{2}h\nu_1^+ + h\nu_2^+$; rotation, $RT$; potential energy, $V_0$; translation of center of mass, $\frac{3}{2}RT$. The average energy of the reactants contains vibration, $\frac{1}{2}h\nu_1$; rotation, $RT$; translation in the center-of-mass system, $3RT/2$; and translation of center of mass, $3RT/2$. Thus,

$$E_a = V_0 + \tfrac{1}{2}h(\nu_1^+ - \nu_1 + 2\nu_2^+) - \tfrac{1}{2}RT. \quad (7)$$

The $E_j^+$ in (6) is $(I/I^+)\ E_j$, i.e., about $(I/I^+)RT$ in thermal systems, which is about $\frac{1}{6}RT$ for the $H+H_2$ reaction and can then be neglected. We then obtain

$$E_a = \Delta - \tfrac{1}{2}RT. \quad (8)$$

When the vibrations are excited thermally in the activation energy studies, a thermal term $\langle \epsilon_1^+ \rangle - \langle \epsilon_1 \rangle + \langle \epsilon_2^+ \rangle$ should be added to the right sides of (7) and (8). A thermal correction can also be computed for $\Delta$ using Eq. (1). It will be small if $\Delta$ is measured photochemically at low temperatures.

Recently, a threshold energy for the reaction

$$D + H_2 \rightarrow DH + H \quad (9)$$

has been reported.[16] The value (about 8 kcal mole$^{-1}$) is close to that found[17] for the activation energy (about 7.5 kcal mole$^{-1}$ around 400°K). Such agreement with Eq. (8) is well within the experimental error.

Expressions for the relation between threshold and activation energy for reactions for which a more classical treatment suffices could also be obtained from Eqs. (1) and (2), the result being sensitive to the extent of about 1 kcal mole$^{-1}$ to that of the detector. With this uncertainty the result is very similar to (8).

At lower temperatures the activation energy would be sensitive to tunneling (for evidence see Ref. 17) and perhaps to the nonadiabatic leak. (The tunneling effect could swamp the leak effect.) With a very sensitive detector the threshold energy could also be sensitive to tunneling and perhaps to nonadiabatic leak. These corrections can be calculated with the aid of equations present or derivable from those in Refs. 1, 6(b), and 6(c). We omit them here.

[15] Compare R. C. Tolman, J. Am. Chem. Soc. **47**, 2652 (1925). For our purposes the argument given there for bimolecular reactions should be replaced by one paralleling exactly his argument for unimolecular reactions. An equilibrium distribution of reactants' states is assumed.

[16] A. Kupperman and J. M. White, J. Chem. Phys. **44**, 4352 (1966); J. M. White, Ph.D. thesis, University of Illinois, June 1966.

[17] B. A. Ridley, W. R. Schulz, and D. J. LeRoy, J. Chem. Phys. **44**, 3344 (1965). The value of ~7.5 kcal mole$^{-1}$ was estimated from Fig. 2 at low $1/T$.

## VI. REMARK ON TESTS OF ACTIVATED-COMPLEX THEORY

Existing justification of activated-complex theory[11] rests on an adiabaticity for all degrees of freedom (exclusive of the reaction coordinate). (Justifications also exist based on a "compound nucleus" model for the activated complex,[18] but current computer-calculated trajectories do not support the idea of long-lived complexes. They would occur if there were a sufficiently deep potential well in the activated-complex region.)

The adiabatic-based justification,[11] stripped of any curvilinear trappings is straightforward (see particularly Eliason and Hirschfelder[11]). The adiabatic aspect is apparently still largely unknown to some active researchers in the field and the argument is recalled briefly in Appendix III, emphasizing this point, freed as much as possible from notational encumbrances.

In the present instance the argument in favor of an adiabatic assumption for the formation of the symmetric stretching mode has been noted earlier, as well as the uncertainty that the other modes are strictly adiabatic. In the reaction-cross-section theory used in the present paper, we have not explicitly assumed an adiabaticity for those other modes, except as required by angular-momentum conservation. Instead, a distribution about an adiabatic value might suffice to fulfill the starting equation, Eq. (2) of Ref. 1.

The present agreement between calculated and computer-calculated $\sigma_{vjp}$'s, as well as the less stringent agreement[12] of Eq. (2) of Ref. 1 with the computer data, support the activated-complex rate equation in the thermal region, though not yet the existing justifications of that equation. For this purpose one needs an analysis of computed-calculated reaction probabilities[12] $w_{lvnp}{}^J$ and of other quantities.[6d]

## APPENDIX I: RELATION BETWEEN ENERGY AND CLASSICAL ACTION FOR ANHARMONIC OSCILLATORS

### A. Nondegenerate Vibration

The action $J$ is given by

$$J = \oint p_x dx, \quad (A1)$$

where $x$ is the oscillator-displacement coordinate and $p_x$ is $[2\mu(E-V)]^{1/2}$. When a quartic anharmonic term occurs,

$$V(x) = \tfrac{1}{2}kx^2 + ax^4, \quad (A2)$$

and the expansion of $p_x$ for small $a$ leads to

$$J = \oint [2\mu(E - \tfrac{1}{2}kx^2)]^{1/2} dx - \mu a \oint x^4 [2\mu(E - \tfrac{1}{2}kx^2)]^{-1/2} dx. \quad (A3)$$

[18] Compare B. C. Eu and J. Ross, J. Chem. Phys. **44**, 2467 (1966).

Contour integration[19] of these two terms yields

$$J=(E/\nu)-(3\nu a/2k^2)\,(E/\nu)^2. \qquad \text{(A4)}$$

Equation (A4) agrees with the result[20] of quantum-mechanical perturbation theory for a nondegenerate vibration, as it should, when one sets $J\cong v+\frac{1}{2}$ and replaces (with no error to order $a$) the $(E/\nu)^2$ by $J^2$.

### B. Doubly Degenerate Bending Vibration

The Hamiltonian is

$$H=[(p_x^2+p_y^2)/2\mu]+V(r), \qquad \text{(A5)}$$

where $x$ and $y$ are components of the oscillator displacement and $r$ is $(x^2+y^2)^{1/2}$. If $r$ and $\phi$ are new coordinates ($x=r\cos\phi$, $y=r\sin\phi$), $H$ becomes

$$H=\frac{p_r^2+(p_\phi^2/r^2)}{2\mu}+V(r). \qquad \text{(A6)}$$

The action $J_\phi$, equal to $\oint p_\phi d\phi$, is $2\pi p_\phi$ since $p_\phi$ is constant. Thus, the action $J_r$, equal to $\oint p_r\,dr$ is, on expansion of $p_r$ for small $a$,

$$J_r=\oint\left[2\mu E-\mu kr^2-\left(\frac{J_\phi}{2\pi r}\right)^2\right]^{1/2}dr$$

$$-\mu a\oint r^4\left[2\mu E-\mu kr^2-\left(\frac{J_\phi}{2\pi r}\right)^2\right]^{-1/2}dr. \qquad \text{(A7)}$$

Contour integration of these two terms yields

$$J=(E/\nu)-(\nu a/2k^2)[3(E/\nu)^2-J_\phi^2], \qquad \text{(A8)}$$

where $J=J_r+J_\phi$.

Since $|J_\phi|$ does not exceed $J$ and averages about $J/2$, and since $(E/\nu)^2\cong J^2$, the term in brackets is about $2.75(E/\nu)^2$. Thus, a comparison of (A4) and (A8) shows that the function $E(J)$, where $J$ is the principal action, is essentially the same for the nondegenerate and doubly degenerate bending vibration.

The function $E(J)$ may be obtained from (A4) or (A8). Alternatively, since $E$ has been calculated exactly as a function of the vibrational quantum number $v_1$ for a nondegenerate oscillator, one may merely replace $v_1+\frac{1}{2}$ in the latter by $J$ and so obtain $E(J)$, as in Appendix I.C below. This same $E(J)$ can then be used for the doubly degenerate bending oscillator, with relatively small errors for our purpose [e.g., neglect of $J_\phi^2$ in Eq. (A8)].

For a doubly degenerate *quantum* oscillator, if the dependence of $E$ on all but the principal quantum number $v_3$ is neglected, the function $E(v_3)$ could be obtained from the above function $E(J)$ by replacing $J$ by its equivalent for a degenerate oscillator $(v_3+1)h$. (The latter equivalence is exact for the harmonic oscillator.) However, for our present purposes we do not need $E(v_3)$.

### C. Exact Quantum Result for a Nondegenerate Oscillator

In Eq. (A10) below, the symbol $m$ was used to replace $v_1+\frac{1}{2}$, where $v_1$ is the quantum number of the nondegenerate vibration.

The eigenvalues of the harmonic-quartic oscillator are given in Ref. 9. The potential-energy function is $\frac{1}{2}kx^2+ax^4$, and the Hamiltonian $H$ is written in terms of another one, $H_\alpha$. The relation between the two, after some manipulation, is found to be

$$H=\tfrac{1}{4}h\nu(1-\alpha)^{-1/2}H_\alpha, \qquad \text{(A9)}$$

where $\alpha/(1-\alpha)=(a h\nu/k^2)^{2/3}$ and $\nu=$frequency when $a$ vanishes. The eigenvalues of $H_\alpha$ are tabulated as $\lambda_\alpha$.

For our purposes, an approximate formula of McWeeny and Coulson,[21] checked by numerical methods in Ref. 9, is quite accurate. One finds, thereby, that the eigenvalues of $H$ are $y$ where

$$y=\tfrac{1}{4}mh\nu(3x_r+x_r^{-1}), \qquad \text{(A10)}$$

and $x_r$ is the real root of

$$x^3-x-6[\alpha/(1-\alpha)]^{3/2}m=0. \qquad \text{(A11)}$$

[In (A11) we neglected a term $\frac{1}{2}$ relative to $m^2$, since $m$ is large for the significant parts of Fig. 1.]

To obtain a plot of $m$ versus $y$, $y$ and $m$ were each calculated as a function of a third variable $x_r$ using (A10) and (A11). The anharmonicity term $a/k^2$, needed for the evaluation of $\alpha/(1-\alpha)$, was calculated from the readily derived result

$$(V-V_h)/V_h^2=4a/k^2, \qquad \text{(A12)}$$

where $V_h$ is the harmonic term $\frac{1}{2}kx^2$ and $V$ is the actual potential function in $H$. Since $V$ was about 0.40, 0.80, and 2.75 eV when the bond angle was $\pi$, $5\pi/8$, and $\pi/3$ (Ref. 22, Fig. 2), and since $h\nu$ is 2.80 kcal/mole one finds $[\alpha/(1-\alpha)]^{3/2}=a h\nu/k^2\cong 0.021$. (At a bond angle of $5\pi/8$, $V$ was taken equal to $V_h$.)

### D. Calculation of $N^+_{\rm vib}(y)$

The exact classical expression for $N^+_{\rm vib}(y)$ is $J^2/2h^2$ when the dependence of $E$ on $J_\phi$ is neglected. Using the plot of $m$ versus $y$ in Appendix I.C, setting $J=mh$, $y=E_p-V_e$ in (A10), and $y=E_p-V_e-E_j^+$ in (A10), $N^+_{\rm vib}(y)$ was calculated for Eqs. (1) and (2).

The correction of $\sigma_{vnp}$ for anharmonicity was 35% at the highest velocity (1.95), about 17% at a velocity of 1.40, 5% at a velocity of 1.05, etc.

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[19] We use a method described by M. Born, *The Mechanics of the Atom* (Frederick Ungar Publ. Co., New York, 1960), pp. 303ff; H. Goldstein, *Classical Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1950), pp. 302–303.

[20] L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., Inc., New York, 1935), p. 161, Eq. (23–30).

[21] R. McWeeny and C. A. Coulson, Proc. Cambridge Phil. Soc. **44**, 413 (1948).

[22] R. N. Porter and M. Karplus, J. Chem. Phys. **40**, 1105 (1964).

## APPENDIX II: CASE OF LARGE BENDING ANGLES. LIMITING $\sigma_{vjp}$

At high energies large bending angles occur and a simple Cartesian expression for the kinetic energy of the bending modes no longer suffices. The actual kinetic energy is used below to calculate the partition function and, thereby, the limiting value of $\sigma_{vjp}$ at high energies. For simplicity, rotation–vibration interaction is neglected in the present paper.

The three atoms in the $H_3$ complex are denoted in sequence by 1, 2, and 3. The doubly degenerate bending motion can be discussed in terms of a set of axes, so chosen that $x_1=x_3=-\frac{1}{2}x_2$, $y_1=y_3=-\frac{1}{2}y_2$, $z_1=-z_3$, and $z_2=0$. The angular momentum about the $x$ and $y$ axes and momentum of the center of mass are seen to vanish in this coordinate system.

The angle which the 1–2 bond (or 2–3) makes with the $z$ axis is denoted by $\theta$ and the angle which the plane of the three atoms makes with $xz$ plane is denoted by $\phi$. The 1–2 and 2–3 bond lengths are each denoted by a fixed length $R$ in this symmetrical complex, for purposes of discussing the bending mode. The transformation corresponds to: $x_1-x_2=R\sin\theta\cos\phi$, $y_1-y_2=R\sin\theta\sin\phi$, $z_1-z_2=R\cos\theta$.

The kinetic energy $T$ is

$$m_{\mathrm{H}}\sum_{i=1}^{3}\tfrac{1}{2}(x_i^2+y_i^2+z_i^2),$$

where $m_{\mathrm{H}}$ is the mass of the H atom. Upon transforming these Cartesian coordinates to the new coordinates $R$, $\theta$, $\phi$, by introducing the above constraints one obtains (A13), where $I^+=2m_{\mathrm{H}}R^2$:

$$T=(I^+/6)[(1+2\sin^2\theta)\dot{\theta}^2+\sin^2\theta\dot{\phi}^2]. \qquad \text{(A13)}$$

From (A13) $p_\theta$ and $p_\phi$ may be calculated as $\partial T/\partial\dot{\theta}$ and $\partial T/\partial\dot{\phi}$, respectively.

The partition function (p.f.) for the bending modes is

$$\text{(p.f.)}=\int\cdots\int\exp\left(\frac{-H}{kT}\right)\frac{dp_\theta dp_\phi d\theta d\phi}{h^2}, \qquad \text{(A14)}$$

where

$$H=\frac{[p_\theta^2/(1+2\sin^2\theta)]+(p_\phi^2/\sin^2\theta)}{2I^+/3}+U(\theta). \qquad \text{(A15)}$$

Integration yields

$$\text{(p.f.)}=\frac{kTI^+}{3\hbar^2}\int_0^{\pi/2}\sin\theta(1+2\sin^2\theta)^{1/2}\exp\left(\frac{-U}{kT}\right)d\theta. \qquad \text{(A16)}$$

The density of bending mode states $\Omega(E)$ of energy $E$ is obtained from (A16) by Laplace transform techniques.[23] $N^+_{\mathrm{vib}}(y)$ is

$$\int_0^y\Omega(E)dE.$$

To obtain $\Omega(E)$ at low energies only the behavior of (A16) at low $T$ is relevant. Here, $U$ can be replaced by $\frac{1}{2}\kappa\theta^2$, where $\kappa$ is a force constant, and $\sin\theta$ can be replaced by $\theta$, and $(1+2\sin^2\theta)$ by 1. Thereby, one obtains the usual harmonic-oscillator expression $(kT/h\nu)^2$, where the bending frequency $\nu$ is[24] $(1/2\pi)(3\kappa/I^+)^{1/2}$. From this (p.f.) $\Omega(E)$ is found to be $E/(h\nu)^2$ and $N^+_{\mathrm{vib}}$ to be $y^2/2(h\nu)^2$.

To obtain $\Omega(E)$ at high energies, only the behavior of (A16) at high $T$ is needed. Then, because of the anharmonicity at a high enough energy $U$ can be taken as zero in some interval $(0,\theta_0)$ and infinite outside. Thereby, at high $T$, Eq. (A16) yields

$$\text{(p.f.)}=(kTI^+/2\sqrt{2}h^2)(\Psi_1-\Psi_0-\tfrac{1}{2}\sin2\Psi_1+\tfrac{1}{2}\sin2\Psi_0), \qquad \text{(A17)}$$

where $\cos\Psi_0=(\frac{2}{3})^{1/2}$ and $\cos\Psi_1=(\frac{2}{3})^{1/2}\cos\theta_0$.

By a Laplace transform method[23] $\Omega(E)$ is found to be the coefficient of $kT$ in (A17) and $N^+_{\mathrm{vib}}(y)$ to be $y$ times that. The corresponding value of $\sigma_{vjp}$, obtained from (1) is (A18), since $\mu$ is $2m_{\mathrm{H}}/3$:

$$\sigma_{vjp}=\Gamma\pi R^2(I^+\sigma/I\sigma^+)(3/4\sqrt{2})$$
$$\times(\Psi_1-\Psi_0-\tfrac{1}{2}\sin2\Psi_1+\tfrac{1}{2}\sin2\Psi_0)[1-(V_e/E_p)]. \qquad \text{(A18)}$$

The angle term in brackets varies roughly as $\theta_0^2$, being $0.025\pi$, $0.108\pi$, and $0.455\pi$, when $\theta_0$ is $\pi/8$, $\pi/4$, and $\pi/2$, respectively. The numerical value of all but the last two factors is 56.5 a.u. From the published potential energy surfaces, there is a cusp which makes entrance through the activated-complex region improbable if the angle of deviation of $H_3$ from linearity, $\gamma$, is as much as $2\pi/3$. By definition $\theta$ is half $\gamma$, so the corresponding maximum value of $\theta$, $\theta_0$, would be $\pi/3$. There is a perceptible beginning of this cusplike behavior when $\gamma$ is $\pi/2$, so $\theta_0$ lies in the interval $\pi/3$ and $\pi/4$. Thus, if $\theta_0$ is $\pi/4$, $\sigma_{vjp}(\max)$ is 19.2 a.u., which is three times the expected extrapolation of the computer values.

It is of interest to compare the values with the well-known hard-sphere-collision-theory value. The latter can be recovered from Eq. (1) by noting that the internal degrees of freedom which contribute to $N^+_{\mathrm{vib}}$ in that case are the two rotations of BC. Thereby,

$$N^+_{\mathrm{vib}}=\int_0^{K_{\max}}2KdK=K_{\max}^2,$$

[23] See C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958), p. 57.

[24] $\nu$ is obtained as follows: First, one finds the action $J_\phi=2\pi p_\phi$. Next by contour integration (compare Appendix I) one finds $J_\theta=-J_\phi+2\pi E(I^+/3\kappa)^{\frac{1}{2}}$. The frequency for the bending motion $\nu(=\nu_\theta)$ is defined in the usual way (Goldstein,[19] p. 293) as $\partial E/\partial J_\theta$, and so equals $(1/2\pi)(3\kappa/I^+)^{\frac{1}{2}}$.

where $K$ is the rotational quantum number of BC in the hard-sphere-collision-theory "activated complex," and $K_{max}$ is the maximum $K$ for the given $E_p - V_e$ ($K^2_{max}\hbar^2/2I = E_p - V_e$). For $I^+$ we have $\mu\sigma_d^2$ in this case; $\sigma_d^2$ is the collision diameter. $\sigma^+$ and $\sigma$ are unity as before. However, $\Gamma$ is unity instead of 2, in the hard-sphere case, since the two resulting reaction paths, one to form AB and the other to form AC, become competitive rather than additive. In this way one obtains from Eq. (1) the value $\pi\sigma_d^2\ (1 - V_e/E_p)$ for the hard-sphere reaction cross section. According to the potential-energy surface, interaction occurs when $\sigma_d \cong (\frac{1}{2}\ 1.5 + 3) = 3.75$ a.u., yielding a value of 44 a.u. for the limiting hard-sphere cross section.

## APPENDIX III: ADIABATIC JUSTIFICATION OF ACTIVATED-COMPLEX THEORY

If the distribution of reactants is a Boltzmann one, the probability of finding the reactants in a vibrational–rotational–orbital state $n$ and in phase space region $dxdp_x$ ($x$ is reaction coordinate and $p_x$ is conjugate momentum) is

$$\frac{dxdp_x}{h}\,\frac{\exp(-E/kT)}{Q}$$

in a center-of-mass system. $Q$ is the reactants' partition function in that system and $E$ is their total energy. When the reactants are far apart, $x$ is simply the distance between their centers of gravity.

The corresponding probability per unit $x$ is obtained by dividing by $dx$, and the corresponding contribution to the reaction rate constant is obtained by multiplying with the velocity $\dot{x}$ and with the transmission coefficient $\kappa(E,n)$, and finally by integrating over all $E$ and summing over all $n$. Since $E$ is the sum of $E_n$ (the vibration–rotation–orbital energy of reactants in state $n$) and of $p_x^2/2\mu$, where $\mu$ is their reduced mass, $dE$ is $p_x dp_x/\mu$, i.e., $\dot{x}dp_x$, at a given $n$. The expression for $k_{rate}$ becomes

$$k_{rate} = \sum_n \int_E \kappa(E, n)\ \exp\left(\frac{-E}{kT}\right)\frac{dE}{hQ}. \qquad \text{(A19)}$$

If an adiabaticity existed for all degrees of freedom, one would have a 1:1 correspondence between states in the activated-complex region and those of the reactants:

$$E = E_n + (p_x^2/2\mu) = E_n^+ + E_{tr}^+, \qquad \text{(A20)}$$

where $E_n^+$ is the rotation–vibration energy of the activated complex and $E_{tr}^+$ is its kinetic energy along the reaction coordinate. Introduction of (A20) into (A19), treatment of the reaction coordinate as classical [i.e., replacing $\kappa(E, n)$ by 1 if $E_{tr}^+ \geq 0$, and by 0 otherwise], and integration yields the usual activated-complex theory expression

$$k_{rate} = \frac{(kT/h)Q^+}{Q}, \qquad \text{(A21)}$$

where $Q^+$ is $\sum_n \exp(-E_n^+/kT)$. [A $\kappa$ could have been left in (A19) for tunneling purposes.]

In the classical version, the summations over quantum states can be replaced[12] by integrations over angle-action variables and $E_n^+$ by $E^+(J_i)$. For example,

$$Q^+ = \int \exp\left[-\frac{E^+(J_i)}{kT}\right]\prod_{i=1}^{N-1} dJ_i dw_i/h^{N-1}, \qquad \text{(A22)}$$

$N$ is the number of degrees of freedom in the center-of-mass system. Integration over the angle variables $w_i$ contributes a factor of unity.